



# High durable poly(vinyl alcohol)/Quaterized hydroxyethylcellulose ethoxylate anion exchange membranes for direct methanol alkaline fuel cells

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## HIGHLIGHTS

- PVA/QHECE hydroxyl anion conducting membranes have been developed.
- The membranes display the high alkaline stability in 6.0 M KOH at 80 °C.
- The excellent dimensional stability is achieved in water and methanol solution at 90 °C.
- The membrane shows methanol permeability of 1/19 of Nafion<sup>®</sup> 115<sup>®</sup>.
- A preliminary fuel cell test gives a power density of 4.6 mW cm<sup>-2</sup> at room temperature.

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## ABSTRACT

Novel alkaline anion-exchange membranes composed of chemically cross-linked poly(vinyl alcohol) modified quaternized hydroxyethylcellulose ethoxylate (PVA/QHECE) are prepared. The hydroxide conductivity ( $\sigma_{OH^-}$ ), water and methanol uptakes, ion exchange capacity (IEC), mechanical property, dimensional and alkaline stabilities of PVA/QHECE membranes are measured to evaluate their applicability in direct methanol alkaline fuel cells (DMAFC). The effects of cross-linking time, membrane composition and catalyst dosage ( $H^+$ ) on membrane  $OH^-$  conductivity are studied using AC impedance technique. FTIR, SEM and TG analysis are used for structural characterization of these membranes. It is found that the  $OH^-$  conductivity of the membranes increases with temperature and reaches up to  $7.5 \times 10^{-3} \text{ S cm}^{-1}$  at 90 °C but no apparent changes on both water uptake and methanol uptake with temperature. The methanol permeability coefficients of the membranes are in the range of  $1.26 - 1.72 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at 25 °C. In addition, the PVA/QHECE membranes show the high alkaline stability in hot 6.0 M KOH at 80 °C without losing their integrity and  $OH^-$  conductivity during a week of evaluation. The membrane electrode assembly (MEA) fabricated with PVA/QHECE (= 1:0.25 by mass) gives an initial power density of 4.6 mW cm<sup>-2</sup> using 2.0 M methanol and 2.0 M KOH as the fuel and O<sub>2</sub> as oxidant at room temperature.

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## 1. Introduction

It is commonly believed that polymer electrolyte membrane fuel cells are destined to become an effective energy alternative, particular to proton-exchange membrane (PEM) fuel cells [1].

Among which the direct methanol fuel cells (DMFCs) are promising candidate as energy sources for transport and other portable applications, due to their high energy density, simplicity in the system structure, easy storage, supply and transport of fuels, no need for fuel reforming or humidification [2]. However, this fuel cell exhibits several significant disadvantages including slow electrode kinetics, CO poisoning of expensive Pt-based electrocatalysts, the high cost of membranes (such as Nafion<sup>®</sup>) and high fuel permeability (methanol).

To solve these problems, recently, great interests have been evoked on alkaline membrane fuel cells (AMFCs). These cells use the anion-exchange membranes to displace the proton-exchange

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membranes with  $\text{OH}^-$  anions instead of  $\text{H}^+$  ions. When the operational environment is alkaline, methanol oxidation is faster than that in an acidic media which allows the use of non-precious metal electrocatalysts such as silver catalysts [3] and perovskite-type oxides [4]. In addition, the water management is improved due to the electro-osmotic drag transporting water away from the cathode, thus the so-called alcohol ‘crossover’ problem is highly reduced because of the opposite movement of  $\text{OH}^-$  anions to the movement of  $\text{H}^+$  ions in acidic membrane [4–6].

To date, several new alkaline anion-exchange membranes (AAEMs) have been evaluated for use in direct methanol alkaline fuel cells (DMAFCs), where the membranes are constructed mainly from copolymers whose quaternized comonomers feature an anion as the charge carrier, such as polysulfone [7,8], fluorinated polymers including poly(ethylene-co-tetrafluoroethylene) (ETFE) and poly(vinylidene fluoride) (PVDF) [6,9], copolymer of 4-vinylpyridin and styrene [10], poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) [11] and polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene [12]. The basic requirements of an AAEM for use in DMAFCs is that it should have good mechanical, thermal and chemical stability and low methanol permeability besides the high  $\text{OH}^-$  conductivity. However, these polymers are generally of high price and, their quaternization is complex process, which is even very toxic and carcinogenic [13].

Cellulose is a natural and low-cost biopolymer [14]. It has many excellent properties such as high water holding capacity, biodegradability, high tensile strength and, good mechanical and thermal property [15]. The hydroxyl groups on its backbone ensure a high selectivity for water in the pervaporative separation of alcohol–water mixtures. Cellulose blends with synthetic polymer such as polyvinyl alcohol (PVA) [16] had been studied extensively as biodegradable polymer blends because of the good miscibility between these components. However, the studies of cellulose used for fuel cell application are very few [17,18]. QHECE, a quaternized hydroxyethylcellulose ethoxylate, can offer anions as charge carriers conducting hydroxide ( $\text{OH}^-$ ). Considering the anion-exchange groups in QHECE, it should be possible to apply QHECE to alkaline anion-exchange membrane fuel cells. However, since QHECE is a highly water-soluble quaternized copolymer, a major research objective is to fix the QHECE in stable structures while maintaining its high  $\text{OH}^-$  conductivity. Chemical cross-linking is a highly versatile method to create and modify polymers, in particular, to limit the swelling and suppress methanol permeability yielding the dimensional and thermal stability of the membranes [19–25]. The alkaline stability, and the  $\text{OH}^-$  conductivity can also be improved by adjusting the cross-linking density of the membranes prepared [23]. Besides, as one of the chemical modification methods, the blending technique is an extremely promising approach due to its potential for combining the attractive features of each blend component while at the same time reducing their deficient characteristics. Therefore, the method simplicity distinguishes it from the existing techniques, allowing the polymer electrolyte membranes (PEMs) to be cost-effective [26,27].

Based on the above conception, in this article, a series of cost-effective PVA/QHECE composite membranes were prepared by blending and chemical cross-linking modifications. QHECE was chosen as the cationic polyelectrolyte for the fabrication of membranes for its dual function both as an alcohol barrier and an  $\text{OH}^-$  conductor. PVA was chosen as the polymer matrix for its perfect methanol barrier property and chemical stability with excellent film forming property [28,29]. To avoid the poor stability in aqueous solutions, PVA was insolubilized by chemical cross-linking reactions. The cross-linked structure was obtained through the reaction of the hydroxyl groups ( $-\text{OH}$ ) of PVA with the aldehyde groups ( $-\text{CHO}$ ) of glutaraldehyde cross-linker in the

presence of a strong acid. Structures of QHECE, PVA and PVA/QHECE network are illustrated in Fig. 1. The membrane characteristics including  $\text{OH}^-$  conductivity, ion exchange capacity, water uptake, methanol permeability, mechanical property, thermal behavior, dimensional and alkaline stabilities were addressed to evaluate their applicability in direct methanol alkaline fuel cells.

## 2. Experimental

### 2.1. Materials and membrane preparation

A stock 10 wt% PVA (99% hydrolyzed, average molecular weight  $M_w = 86,000$ – $89,000$ , Aldrich) aqueous solution was prepared by dissolving PVA in distilled water at  $90^\circ\text{C}$ . QHECE (Aldrich) was separately prepared, then QHECE and PVA solutions were mixed in different proportions under stirring for at least 2 h to make sure that the new solution was completely homogeneous. After degassed in a vacuum chamber, the solutions were poured into the plastic dishes, and dried in the ambient conditions. Then the samples of rectangular pieces of membranes (ca.  $1.5 \times 2$  cm) were soaked in a reaction solution consisting of 10 wt% glutaraldehyde (GA) and small amount of HCl in acetone at  $30^\circ\text{C}$  for chemical cross-linking. Before the use, the membrane was treated by immersing in 1.0 M KOH solution overnight to convert it from  $\text{Cl}^-$  form into  $\text{OH}^-$  form, then washed with deionized (D.I.) water until pH neutral and finally stored in D.I. water for measurements. Transparent, flat membranes (PVA/QHECE) were obtained with a thickness of about several tens of micrometers ( $40$ – $60\ \mu\text{m}$ ). The membrane abbreviations were listed in Table 1.

### 2.2. Membrane characterizations

The molecular structure of chemically cross-linked PVA/QHECE composite membranes was characterized by Fourier transform infrared (FTIR) spectroscopy. The infrared spectrometer (Tensor 27, Bucker) equipped with attenuated total reflectance (ATR) instrument was used to obtain the spectrogram with a wavenumber resolution of  $4\ \text{cm}^{-1}$  in the range from  $4000$  to  $500\ \text{cm}^{-1}$ .

Thermal gravimetric analysis (TGA) of membranes was carried out with a TG 209 analyzer (Netzsch). Samples of 5 mg loaded into an alumina oxide pan, were heated from  $25$  to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}\ \text{min}^{-1}$  with  $20\ \text{mL}\ \text{min}^{-1}$  nitrogen gas flowing as protection.

Tensile evaluation was performed on a universal material testing machine (H5K-S, Hounsfield) under ambient condition (room temperature,  $\sim 50\%$  relative humidity) at a speed of  $5\ \text{mm}\ \text{min}^{-1}$  with a  $1000\ \text{N}$  sensor loaded. The mean value was obtained from at least three strip samples with the size of  $1 \times 5\ \text{cm}$ .

The composite morphology was evaluated using an FEI Sirion 200 field-emission scanning electron microscope (SEM) operating at  $5\ \text{kV}$ . Prior to observations, the membrane samples were fractured in liquid nitrogen and sputtered with gold, then examined at  $1000$  and  $20,000$  magnifications.

### 2.3. Ion exchange capacity (IEC), water/methanol uptake and swelling ratio

The ion exchange capacity (IEC,  $\text{meq}\ \text{g}^{-1}$ ) of the membranes was determined using the classical titration method. The composite membrane was soaked in  $100\ \text{mL}$  of  $2.0\ \text{M}$  KOH solution to convert into the  $\text{OH}^-$  form. The membrane was washed with D.I. water to remove excess KOH, then equilibrated with  $25\ \text{mL}$  of  $0.1\ \text{M}$  HCl solution for 24 h. The IEC value was determined from the reduction in acid measured using back titration. The IEC value is defined as mequiv of quaternary ammonium groups per gram of dried sample.

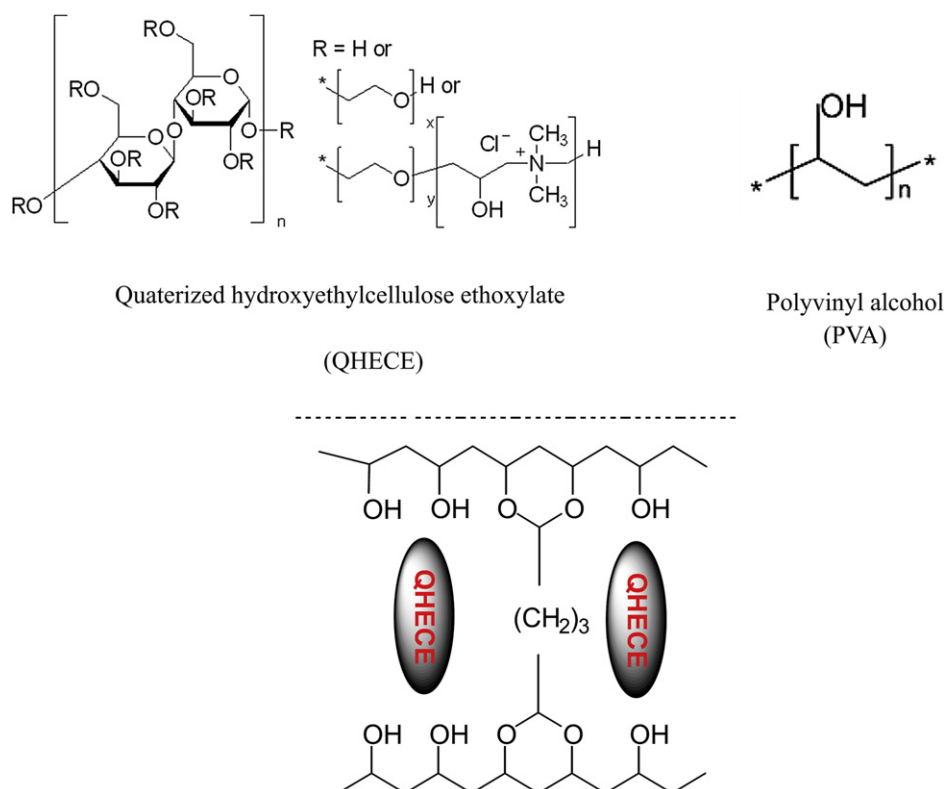


Fig. 1. Structures of QHECE, PVA and chemically cross-linked PVA/QHECE alkaline membranes. 10% GA served as a cross-linking agent.

The swelling of the membranes was evaluated by the water uptake ( $WU$ ) and the methanol uptake ( $MU$ ) of the membranes ( $\text{g g}^{-1}$ ), which was estimated from the mass change before and after the complete dryness of the membrane. A dry membrane was swelled in D.I. water or in 99.8% methanol solution at the controlled temperatures for a day, then the surface water was wiped carefully with a filter paper, and it was immediately weighed. After drying the sample overnight in a vacuum oven at  $60^\circ\text{C}$ , the  $WU$  or  $MU$ , was calculated using the expression:

$$WU \text{ or } MU = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \quad (1)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the masses of the fully hydrated membrane and of the dry membrane, respectively.

The swelling ratio was measured to evaluate the membrane dimensional stability. The membrane samples were immersed in D.I. water or methanol solution in fully hermetic flasks at a constant temperature, then the surface water was carefully wiped out, and quickly measured the length  $L_x$ , width  $L_y$  and thickness  $L_z$  of the membrane sample. After drying the sample overnight at  $60^\circ\text{C}$ , the swelling ratio ( $SR$ ), was calculated using the expression:

$$V = L_x \times L_y \times L_z, \quad SR = (V_{\text{wet}} - V_{\text{dry}}) / V_{\text{dry}} \quad (2)$$

where  $V_{\text{wet}}$  and  $V_{\text{dry}}$  are the volume of the fully hydrated membrane and of the dry membrane, respectively.

#### 2.4. $\text{OH}^-$ conductivity and alkaline resistance stability

The ionic ( $\text{OH}^-$ ) conductivity of the formed membranes was measured by an AC impedance technique using an electrochemical impedance analyzer (CHI760), where the AC frequency was scanned from 100 kHz to 0.1 Hz at a voltage amplitude of 100 mV. Fully hydrated membranes were sandwiched in a Teflon conductivity cell equipped with Pt foil contacts [25]. The membrane was in contact with water throughout the measurement. The impedance was measured by placing the cell in a temperature-controlled chamber under a temperature range of  $20$ – $90^\circ\text{C}$ . The  $\text{OH}^-$  conductivity, ( $\text{S cm}^{-1}$ ), was calculated according to the following equation:

$$\sigma = l / RA \quad (3)$$

where  $l$  is the thickness and  $A$  is the contact area of the sample membrane.

Table 1

Physical–chemical properties of chemically cross-linked PVA/QHECE and those compared with Nafion 115 ( $t = 22 \pm 2^\circ\text{C}$ ).

| PVA/QHECE (by mass) | $WU (\text{g g}^{-1})$ |               | $\sigma (\times 10^3 \text{ S cm}^{-1})$ |               | IEC (meq $\text{g}^{-1}$ ) | $P_M (\times 10^6 \text{ cm}^2 \text{ s}^{-1})$ | Membrane color     | Membrane flexibility |
|---------------------|------------------------|---------------|--|---------------|----------------------------|---|--------------------|----------------------|
|                     | $\text{Cl}^-$          | $\text{OH}^-$ | $\text{Cl}^-$                            | $\text{OH}^-$ |                            |   |                    |                      |
| 1:0.125             | 0.39                   | 0.41          | 0.69                                     | 0.81          | 0.18                       | —   | Transparent        | ○                    |
| 1:0.25              | 0.44                   | 0.60          | 0.71                                     | 1.18          | 0.26                       | 0.126   | Transparent        | ○                    |
| 1:0.5               | 0.62                   | 0.82          | 0.96                                     | 1.21          | 0.41                       | 0.172   | Transparent        | ○                    |
| 1:75                | 0.85                   | 0.90          | 1.15                                     | 1.33          | 0.46                       | —   | Semitransparent    | △                    |
| 1:1                 | 1.43                   | 1.49          | 1.10                                     | 1.18          | 0.52                       | —   | White              | ×                    |
| Nafion 115          | 0.34                   | —             | 0.091 $\text{S cm}^{-1}$                 |               | 0.92                       | 2.35  | Wholly transparent | ○                    |

10% GA as a cross-linking agent. Cross-linking time: 1 h. ○ flexible and toughness; △ a little brittle and phase separation; × very brittle and partially dissolved in water.

The alkaline resistance of the membranes was evaluated by immersing the membranes in hot 6 M KOH at 80 °C for one week. The change  $\text{OH}^-$  conductivity of the membranes was measured at certain time intervals. After complete removal of the free KOH on the membrane surface, the  $\text{OH}^-$  conductivity of the membranes was determined at ambient temperature. The change in  $WU$  of the membranes was also measured after KOH conditioning.

### 2.5. Methanol permeability

Methanol permeability,  $P_M$ , of the PVA/QHECE membranes was measured using a home-made liquid diffusion cell which was composed of two glass compartments, each with a capacity of approximately 80 mL, separated by a vertical membrane (effective area 7.07  $\text{cm}^2$ ) [23]. The membranes were equilibrated in deionized water for at least 24 h prior to the test. One compartment ( $V_1$ ) was filled with a 3.0 M methanol-water solutions ( $\text{CH}_3\text{OH}$ : analytically pure, SCRC). The other one ( $V_2$ ) was filled with pure D.I. water. Methanol was diffused from  $V_1$  to  $V_2$  by the concentration difference between the two compartments, which were well-stirred during the test. The concentration of permeating methanol was measured by gas chromatography (Agilent 7890A GC). Considering very low methanol permeability of the membranes as described below, in this work, the water osmotic contribution was not taken into account for determining the methanol permeability.

### 2.6. Membrane electrode assembly (MEA) fabrication and single-cell performance

The cell configuration: 2.0 M MeOH + 2.0 M KOH | Pt/C | PVA-QHECE (1:0.125 by mass) | Pt/C |  $\text{O}_2$ , was used in a single-cell of ADMFC. Catalyst slurry was prepared by mixing 40% Pt/C (Johnson–Matthey) with 5 wt% Nafion solution (Aldrich) for the ink. The catalyst ink was coated on carbon paper (Toray TGP-H-090) by a spray method to give a metal loading of 0.5  $\text{mg cm}^{-2}$  on both the anode and the cathode. The active electrode area for a single cell test was 4  $\text{cm}^2$ . MEA was fabricated by hot pressing the PVA/QHECE membrane with anode and cathode at 110 °C and 100  $\text{kg cm}^{-2}$  for 3 min. The MEA was inserted into a fuel cell hardware which consisted of graphite block with machined serpentine flow channel and golden current collectors. 2.0 M MeOH + 2.0 M KOH aqueous solution was pumped into the anode channel of the cell with a flow rate 3  $\text{mL min}^{-1}$ . Pure oxygen gas was supplied as the cathode fuel to enter the cathode channel with a gas flow rate 150  $\text{mL min}^{-1}$  through a humidifier held at room temperature under ambient pressure.

## 3. Results and discussion

### 3.1. FT-IR studies

Infrared spectra of PVA/QHECE membranes in different QHECE contents are shown in Fig. 2. It is clear to observe that the absorption peaks between 3300 and 3700  $\text{cm}^{-1}$  are ascribed to the stretching vibration of  $-\text{OH}$  groups from PVA and QHECE. The appearance of a characteristic peak centered at 1647  $\text{cm}^{-1}$  corresponds to the bending vibration of  $\text{C}=\text{N}$  of QHECE and, the peak at 1718  $\text{cm}^{-1}$  is owing to the stretching of carbonyl groups from cross-linked PVA. The latter is ascribed to the ‘free’  $-\text{CHO}$  attached to GA, indicating a reduced accessibility of the reactive groups caused by an increase of the network density [24,25]. With increasing the content of QHECE in membrane, the peak for the absorption bands at 1647  $\text{cm}^{-1}$  (PVA/QHECE = 1:0.125 by mass) became stronger and shifted to lower wave numbers, i.e. 1641  $\text{cm}^{-1}$  (PVA/QHECE = 1:0.25 by mass), 1639  $\text{cm}^{-1}$  (PVA/QHECE = 1:0.5 by mass)

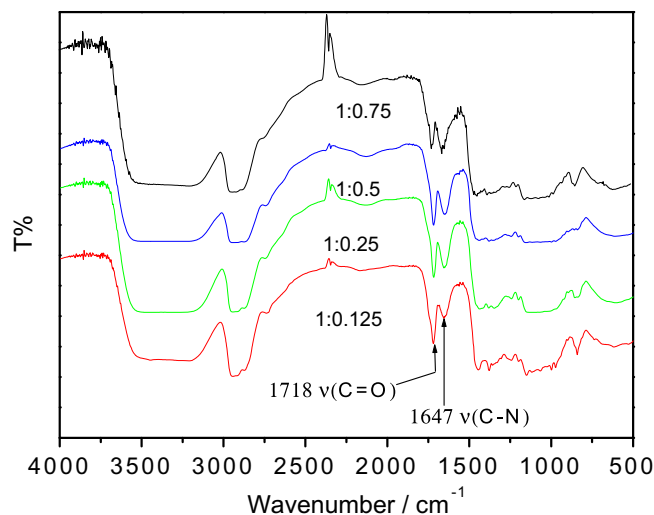


Fig. 2. FTIR spectra of PVA/QHECE alkaline membranes in different content of QHECE.

and 1637  $\text{cm}^{-1}$  (PVA/QHECE = 1:0.75 by mass), respectively. This shift indicates the strong intermolecular hydrogen-bonding effect between  $-\text{OH}$  groups from cationic polyelectrolyte QHECE. On the other hand, the characteristic peak related to carbonyl groups at 1718  $\text{cm}^{-1}$  in PVA/QHECE (1:0.125 by mass) membrane shifted to 1710  $\text{cm}^{-1}$  in PVA/QHECE (1:0.75 by mass) membrane, suggesting further the existence of intermolecular hydrogen bonds between QHECE and  $-\text{OH}$  groups of PVA. The results show that a semi-interpenetrating network (semi-IPN) was constructed between QHECE and PVA two polymers, which may lead to enhanced compatibility between the two polymers with synergistic effect to suppress methanol permeability, increase thermal stability and alkaline resistance stability. This will be discussed thoroughly in the following sections.

### 3.2. The SEM images of PVA/QHECE membranes

Fig. 3 shows the cross-view of the SEM pictures for PVA/QHECE composite membranes both for  $\text{OH}^-$  form and for  $\text{Cl}^-$  form. Small shallow folded cavities were observed to be irregularly distributed in PVA/QHECE membrane (Fig. 3(A)) and became obvious with increasing QHECE content in polymer (Fig. 3(B)). High QHECE content means the high activate anion groups (quaternary ammonium groups) in the neutral polymer matrix which may accounts for the phase separation phenomena in the membranes. Therefore, the compatibility between PVA and QHECE is poor when in so high content of QHECE, and the uniform network structure can't be formed during the chemical cross-linking process. On the other hand, the structures of these membranes become relatively loose due to the formation of these small shallow folded cavities (Fig. 3(B)), which improves the membrane flexibility to a certain extent. Compared to the membrane before ion-exchange ( $\text{Cl}^-$  form), the structure of the membranes after ion-exchange became denser in low content of QHECE (PVA/QHECE = 1:0.125 by mass), due to the formation of hydrogen bond resulting from  $\text{OH}^-$  in the membrane.

### 3.3. Mechanical property

The mechanical property of PVA/QHECE composite membranes was evaluated such as the tensile strength and tensile elongation, and the results are presented in Table 2. It can be seen that when the content of QHECE is less than 33% (PVA/QHECE < 1:0.5 by mass),



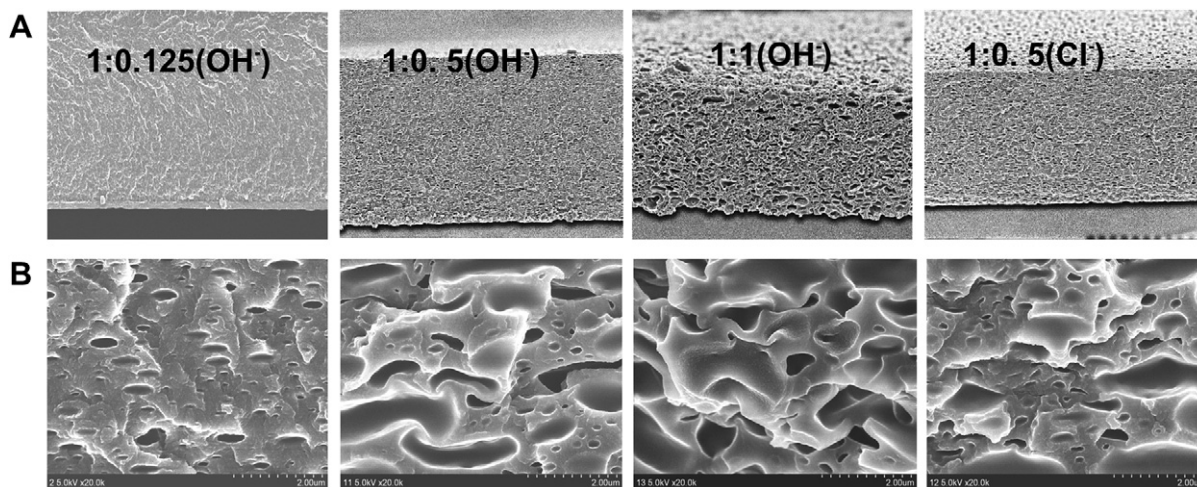


Fig. 3. SEM pictures of the cutview of PVA/QHECE alkaline membranes. (A) (1000×), (B) (20000×).

the tensile strength values are in the range of 29.6–39.8 MPa with the tensile elongation values in the range of 6.45–8.65%. These values are even higher than that of PPO–Br–OH modified with silica [28] and Semi-IPN-21% [29] reported elsewhere, although only the pure aliphatic skeleton in PVA/QHECE membranes. It is interesting to find that in the tested range of membrane compositions (PVA/QHECE = 1:0.125 to 1:0.75 by mass), with increasing the content of QHECE the tensile strength of the membranes decreased, whereas the elongation of the membranes increased. Since QHECE is a polymer with large molecule weight, the structural network in membranes is relatively dense due to the high cross-linking density when the content of QHECE is low. However, with further increasing the content of QHECE, long polymer chains along with the increased hydrophilic groups makes the membrane to absorb more water molecules. All this could act as the effect of the plasticizer, which improves the flexibility of the membranes [22].

### 3.4. Thermal analysis

The TG profiles of the chemically cross-linked PVA/QHECE composite membranes in OH<sup>−</sup> form are shown in Fig. 4. For a good comparison, pristine PVA and chemically cross-linked PVA are also presented in Fig. 4. For pristine PVA before chemical cross-linking, three major weight loss stages are observed at around 25–200, 210–380, and 400–450 °C, respectively. After chemical cross-linking, the onset decomposition temperature is lasted to 330 °C, nearly 80 °C higher than that of pristine PVA before cross-linking. For PVA/QHECE composites, all of the samples display three major weight loss stages at around 25–290, 300–450, and >450 °C, where the onset decomposition temperature (PVA/QHECE = 1:0.125 by mass) is 30 °C lower than that of chemically cross-linked PVA since quaternary ammonium groups on QHECE are more active than PVA network. The initial weight loss of the membranes (25–230 °C) mainly involves the expulsion of water molecules from the

polymer membrane or the moisture absorbed from the air. The total weight loss at this stage is about 5%. The second region (270–450 °C) is attributed to the decomposition of quaternary ammonium groups with a total weight loss about 70%, and the third region (>450 °C) can be ascribed to the splitting of the PVA main chain with a total weight loss about 13%. By changing the content of QHECE from 25% to 75%, no obvious decrease in onset decomposition temperature was observed. This may be due to the strong hydrogen-bonding effect between PVA and QHECE. Furthermore, since QHECE has abundant –OH groups on its molecules, strong hydrogen bonds also forms either from intra- or inter-molecular hydrogen-bonding effects. This, together with the high densely chemical cross-linkage of PVA matrix gives rise to the increased thermal stability of the composite membranes, although the active quaternary ammonium groups in polymer increased with the content of QHECE.

### 3.5. Water uptake (WU), ion exchange capacity (IEC) and ionic (Cl<sup>−</sup> and OH<sup>−</sup>) conductivity

#### 3.5.1. Effect of cross-linking time and catalyst dosage

Fig. 5 shows a typical effect of cross-linking time on both the water uptake and the ionic conductivity (Cl<sup>−</sup>) of PVA/QHECE

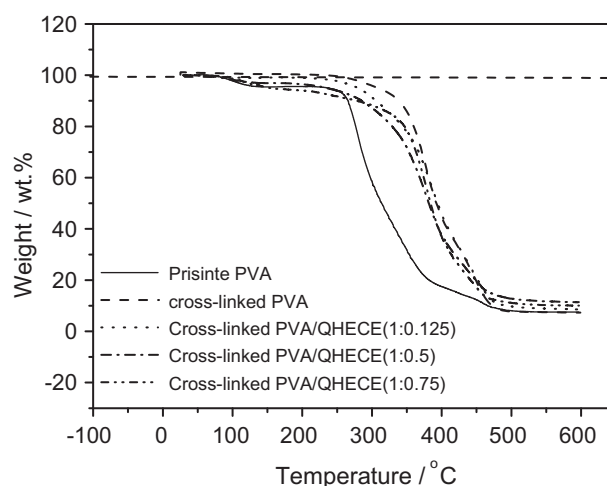
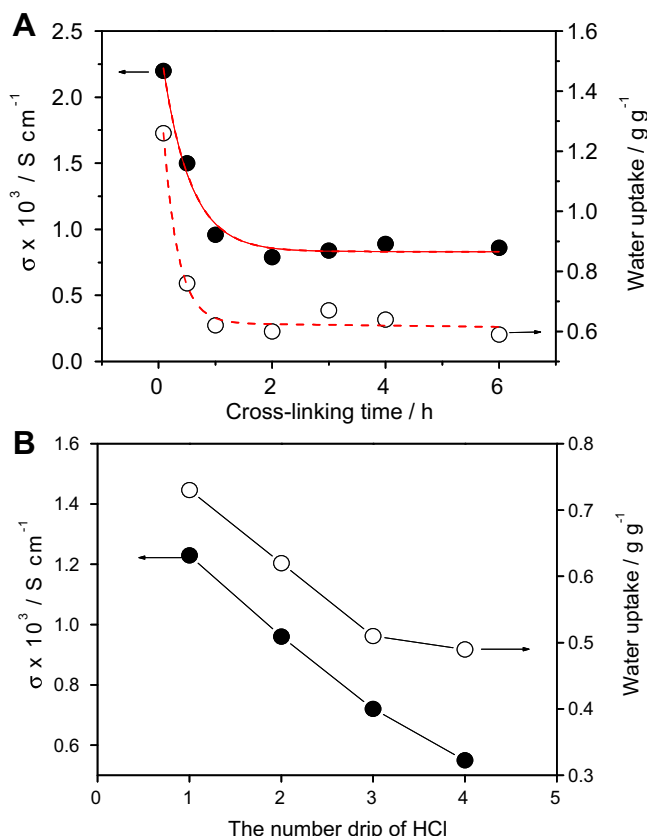


Fig. 4. TG profiles of pure PVA, chemically cross-linked PVA and chemically cross-linked PVA/QHECE alkaline membranes.

**Table 2**  
The mechanical property of chemically modified PVA/QHECE membranes ( $t = 30 \pm 2$  °C).

| PVA/QHECE (by mass) | 1:0.125 | 1:0.25 | 1:0.5 | PPO–Br–OH (7.8% silica) [28] | Semi-IPN-21% [29] |
|---------------------|---------|--------|-------|------------------------------|-------------------|
| TS (MPa)            | 39.8    | 32.1   | 29.6  | 23.5                         | 20.0              |
| $E_b$ (%)           | 6.45    | 7.19   | 8.65  | 5.2                          | 8.1               |

TS–Tensile strength,  $E_b$ –Elongation at break.



**Fig. 5.** Effect of (A) cross-linking time and (B) catalyst (HCl) dosage on water uptake and  $\text{OH}^-$  conductivity of PVA/QHECE alkaline membranes. Membrane composition: 1:0.25 by mass.

membranes with polymer composition of 1:0.5 (by mass) as a typical candidate. Before chemical cross-linking, all of the PVA/QHECE membrane samples could be dissolved in water and converted from a clear, dry membrane to a cloudy, gel-like state just prior to dissolution. After chemical cross-linking, however, using GA as a cross-linker the resultant membranes become robust and flexible when optimizing the membrane composition PVA/QHECE in the appropriate ratios. Obviously, the micro-structure of the membranes becomes denser due to the modification of chemical cross-linking, thus the more hydrophobic property of the membranes emerged leading to decrease in water uptake. The water uptake (WU), expressed as grams of water incorporated per gram of dry membrane, therefore, could be evaluated as a measure of cross-linking density, as will be discussed thoroughly in the following section.

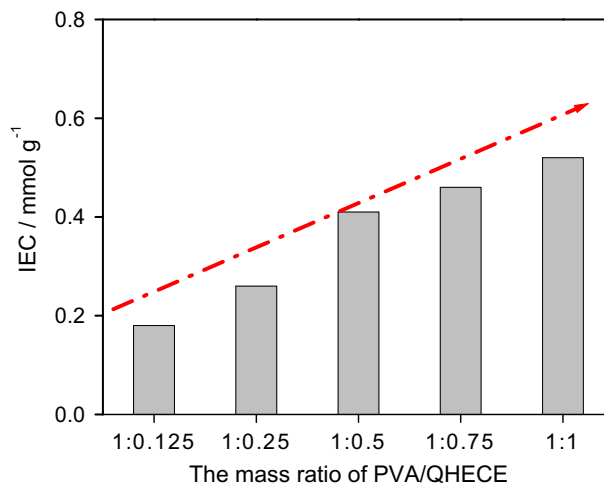
From Fig. 5(A), it can be seen that the cross-linking density of the membranes strongly depends on the cross-linking time. At the initial 1 h cross-linking reaction, the WU decreased significantly accompanied by a sharp decrease in  $\text{Cl}^-$  conductivity due to the reduced water absorption. With a further cross-linking time, both the  $\text{Cl}^-$  conductivity and WU tends to level off, indicating the completed cross-linking reaction. Therefore the optimal reaction time was thus determined as 1 h for all the membrane samples tested. It should be mentioned that hydrochloric acid (HCl) was used to be acted as a catalyst during the cross-linking reaction process. Fig. 5(B) shows a typical effect of catalyst dosage on both WU and  $\text{OH}^-$  conductivity of the PVA/QHECE membranes. Also, the polymer composition of PVA/QHECE = 1:0.5 (by mass) as a typical candidate. From Fig. 5(B), it can be seen that with increasing the dosage of HCl in chemical cross-linking reaction, the WU greatly

decreased from 76% to 49%, accompanied by a linear decrease in  $\text{Cl}^-$  conductivity from  $1.25 \times 10^{-3} \text{ S cm}^{-1}$  to  $3.21 \times 10^{-4} \text{ S cm}^{-1}$  due to large loss of water absorption in the membrane. For obtaining both good mechanical property and reasonable  $\text{OH}^-$  conductivity of the membranes, in this work, the dosage of 0.2% HCl was found to be the best composition for catalyzing the chemical cross-linking reaction. Below or above this dosage, either a so high WU of the membrane (larger than 125%) or brittle membrane was obtained that is not suitable for a practical usage of the membranes.

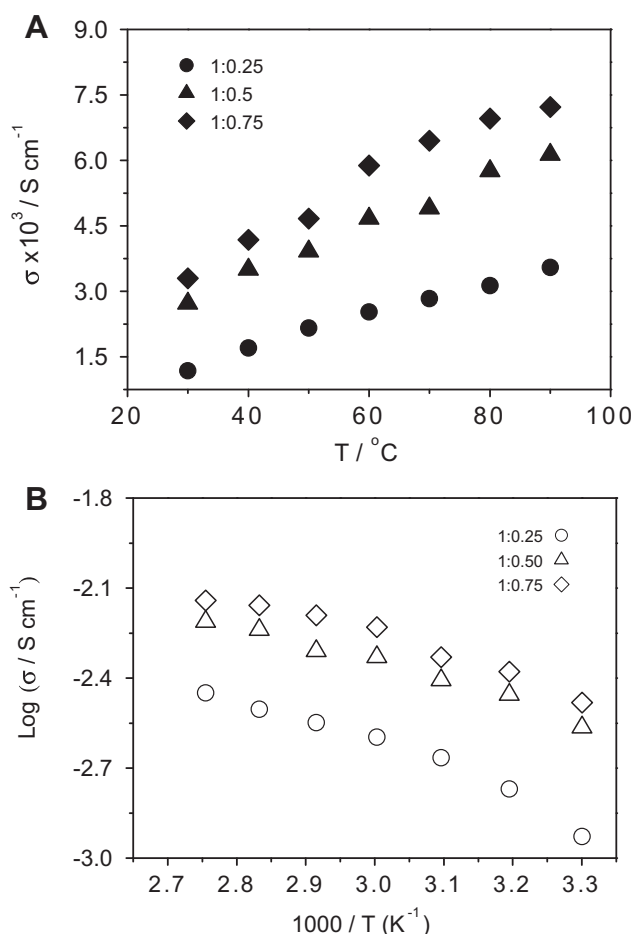
### 3.5.2. Dependence of IEC and $\text{OH}^-$ conductivity on the polymer composition

The IEC value is one of important indices about the membrane performance. In this work, the IEC values of PVA/QHECE membranes are shown in Fig. 6 and Table 1. One can see that the measured IEC values increases with increasing the content of QHECE, and fall in the range of 0.18–0.52 meq g<sup>-1</sup>. The increased IEC values can be explained by the following two facts. One reason is due to the increased quaternary ammonia groups with increasing the content of QHECE in polymer, thus the charge carriers is increased since the number of exchangeable  $\text{OH}^-$  increases. The other reason may be due to the fact that the structure of membrane becomes relatively loose with increasing the content of QHECE in polymer (see Fig. 2). This may provide the more  $\text{OH}^-$  groups entering into the internal structure of the membrane during the ion-exchange process. In short, the alkaline anion conductivity and water uptake is increased with an increase in IEC because of the high density of charge carries and hydrophilic groups ( $-\text{OH}$  groups and  $-\text{NH}_2$  groups in the polymer backbone) in the membranes.

The physicochemical properties of PVA/QHECE composite membranes after chemical cross-linking modifications are summarized in Table 1, including the ionic conductivity ( $\sigma_{\text{Cl}^-}$  and  $\sigma_{\text{OH}^-}$ ) and, water and methanol uptake ( $\text{WU}_{\text{Cl}^-}$  and  $\text{WU}_{\text{OH}^-}$ ). It can be seen that the alkalized membranes ( $\text{OH}^-$  form) showed the higher WU than that of quaternized ones ( $\text{Cl}^-$  form), indicating that  $\text{Cl}^-$  is much less active than  $\text{OH}^-$  on the alkalized polymer when interacting with water molecules [30]. The ionic conductivity values,  $\sigma_{\text{OH}^-}$  are all higher than  $\sigma_{\text{Cl}^-}$ , indicating that the quaternary ammonium groups in QHECE are stable after chemical cross-linking modifications. The  $\text{OH}^-$  conductivity of the membranes increased gradually with an increase in the content of QHECE in membrane, and reached a maximum of  $1.33 \times 10^{-3} \text{ S cm}^{-1}$  as the mass ratio of PVA/QHECE was increased from 1:0.125 to 1:0.75, then slightly decreased with further addition of QHECE, for example, when PVA/



**Fig. 6.** IEC change as a function of membrane composition.



**Fig. 7.** (A) Temperature dependence of  $\text{OH}^-$  conductivity, (B) The  $\log\sigma$  vs.  $1000/T$  plot for PVA/QHECE alkaline membranes.

QHECE being above 1:1. It is noted that the increase in  $\sigma_{\text{OH}^-}$  value is less obvious than that of WU, where the WU of the membranes increased greatly from 41% to 149% with increasing the content of QHECE in polymer. This can be explained by the strong hydrophilic property of quaternary ammonium groups, hydroxyl groups, and cellulose ethoxylate groups in QHECE. All above does not simply give an improved  $\text{OH}^-$  conductivity but rather a dilution of charge carries. Therefore, the mass ratio of PVA/QHECE composition lower than 1:0.75 should be controlled for a practical usage of consideration, whereas the membrane becomes very brittle with mass ratio of PVA/QHECE above 1: 1.

### 3.5.3. Temperature dependence of $\text{OH}^-$ conductivity

Fig. 7 shows the temperature dependences of the  $\text{OH}^-$  conductivity of PVA/QHECE composite membranes, where the membranes are prepared from three different QHECE contents (PVA/QHECE = 1:0.125, 1:0.25 and 1:0.75 by mass), respectively. All the membrane samples exhibited positive temperature–conductivity dependencies in the tested temperature range from

30 to  $90^\circ\text{C}$  (Fig.7(A)). For membrane sample PVA:QHECE = 1:0.75 by mass, its conductivity reached up to  $7.5 \times 10^{-3} \text{ S cm}^{-1}$  at  $90^\circ\text{C}$ . Since the  $\text{OH}^-$  mobility in these membranes is difficult due to the bulky size, it is sensitive to temperature. However, the increased degree in conductivity decreases with increasing the content of QHECE at the same temperature. This result could be supported by the data in Table 1. The apparent activation energy for ion-migration,  $E_a$ , was estimated from Fig. 7(B). Linear regression of natural  $\log\sigma$  vs.  $1/T$  was performed assuming an Arrhenius relationship. The ion transport activation energy,  $E_a$ , derived from the slopes of the Arrhenius plots are  $15.9 \text{ kJ mol}^{-1}$  (PVA/QHECE = 1:0.125 by mass),  $12.0 \text{ kJ mol}^{-1}$  (PVA/QHECE = 1:0.5 by mass) and  $11.8 \text{ kJ mol}^{-1}$  (PVA/QHECE = 1:0.75 by mass), which are similar to the  $E_a$  of Nafion 117 ( $12 \text{ kJ mol}^{-1}$ ) as reported elsewhere [24,25].

## 3.6. Membrane stability

### 3.6.1. Dimensional stability

In Table 3, the swelling ratio (SR) for PVA/QHECE membrane (1:0.125 by mass) both in water and methanol solutions at  $90^\circ\text{C}$  are illustrated to evaluate the dimensional stability of the membranes. The results for Nafion 115® at the same measuring conditions are also compared in Table 3. It can be seen that PVA/QHECE composite membrane showed the SR of 7.8% in water and 22% in methanol solution, whereas 115® showed the SR of 55.5% and 621% in water and methanol solution, respectively. Therefore, it can be concluded that the acetal ring was maintained and did not decompose in this high temperature treatment. It is worth mentioning that Nafion 115® showed a strong swelling behavior especially in  $90^\circ\text{C}$  hot methanol solution, where the dimensional change in area-direction, i.e.  $\Delta S/S$  is nearly 30-fold of PVA/QHECE membrane. On the contrary, PVA/QHECE membrane showed the dimensional change in area-direction all lower than 10% either in water or in methanol solution at  $90^\circ\text{C}$ . In addition, as shown in Table 3, the change in length due to swelling was found to be very different, i.e. almost no change in the directions of both in  $L_x$  and  $L_y$ , but large change in  $L_z$  direction, indicating an anisotropic swelling property of PVA/QHECE membranes. These results suggest that PVA/QHECE composite membranes possess the perfect dimensional stability both in hot water and methanol solution. Compared to Nafion 115® membrane, the PVA/QHECE composite membrane has lower free volume due to stronger hydrogen-bonding effect among QHECE molecules and high dense cross-linkages in PVA matrix. Therefore, the PVA/QHECE membrane is usually less swollen in the presence of methanol and water even at high temperatures, which results in a lower methanol uptake of PVA/QHECE membranes as Fig. 8 showed.

### 3.6.2. Alkaline resistance stability

In Fig. 9, the alkaline resistance stability of PVA/QHECE alkaline membranes was evaluated with both low content of QHECE (1:0.125 by mass) and high content of QHECE (1:1 by mass) by the accelerated experiment, i.e. immersing the membranes in hot 6 M KOH at  $80^\circ\text{C}$ . After complete removal of the free KOH on the membrane surface, the  $\text{OH}^-$  conductivities and the WU of the

**Table 3**

The swelling behavior of chemically cross-linked PVA/QHECE membranes ( $t = 90 \pm 2^\circ\text{C}$ ).

| PVA/QHECE (by mass) | In water                     |                       |                  |        | In methanol                    |                         |                      |        |
|---------------------|------------------------------|-----------------------|------------------|--------|--------------------------------|-------------------------|----------------------|--------|
|                     | $\Delta S$ ( $\text{cm}^2$ ) | $S$ ( $\text{cm}^2$ ) | $\Delta S/S$ (%) | SR (%) | $\Delta S_1$ ( $\text{cm}^2$ ) | $S_1$ ( $\text{cm}^2$ ) | $\Delta S_1/S_1$ (%) | SR (%) |
| 1:0.125             | 0                            | 1.65                  | 0                | 7.8    | 0.13                           | 1.3                     | 10                   | 22     |
| Nafion115           | 0.56                         | 1.6                   | 35               | 55.5   | 3.42                           | 1.2                     | 285                  | 621    |

$S = L_x \times L_y$ ,  $\Delta S = S' - S$ ,  $V = L_x \times L_y \times L_z$ ,  $\Delta V = V' - V$ ,  $SR = \Delta V/V$ . Where  $S'$  and  $V'$  are the data after swelling,  $S$  and  $V$  are the data before swelling.

membranes were determined at ambient temperature. As can be seen in Fig. 9, no decrease in  $\text{OH}^-$  conductivity was observed for PVA/QHECE alkaline membranes either for a low content of QHECE or for a high content of QHECE in the membranes. Compared with those before conditioning in KOH solution ( $8.1 \times 10^{-4} \text{ S cm}^{-1}$  for PVA/QHECE = 1:0.125 by mass, and  $1.18 \times 10^{-3} \text{ S cm}^{-1}$  for PVA/QHECE = 1:1 by mass at  $20^\circ\text{C}$ , respectively), the  $\text{OH}^-$  conductivities of PVA/QHECE membranes are in contrast slightly increased to  $4.38 \times 10^{-3} \text{ S cm}^{-1}$  and  $1.75 \times 10^{-3} \text{ S cm}^{-1}$ , respectively. During the alkaline resistance experiment, the PVA/QHECE membranes were immersed in  $80^\circ\text{C}$  hot KOH solution for one week, hence the membranes swelled and the water content increased, resulting in an increase in the conductivity of the PVA/QHECE membrane. On the other hand, high densely network structure between cross-linked PVA and QHECE effectively suppress the nucleophilic substitution reaction and Hofmann degradation reaction. The above results indicate that the PVA/QHECE membranes exhibit the excellent alkaline stability and could be able to withstand the hydroxide ions attack during the operation of fuel cells.

### 3.6.3. Oxidation stability

To evaluate the oxidative durability of PVA/QHECE alkaline membranes, time dependent measurements of the  $\text{OH}^-$  conductivity in 3% and 10%  $\text{H}_2\text{O}_2$  solutions at an elevated temperature of  $60^\circ\text{C}$  were carried out, respectively. In Fig. 10, the PVA/QHECE (1:0.125 by mass) membrane was tested as a typical candidate. The membrane samples were taken out of the solution at regular intervals and washed with D.I. water for  $\text{OH}^-$  conductivity measurement at room temperature. As can be seen in Fig. 10, no noticeable conductivity change was observed after the membrane sample was treated in 3%  $\text{H}_2\text{O}_2$  solution up to 50 h at  $60^\circ\text{C}$ , and about 12.5% decrease in conductivity was observed after 200 h. When the membrane sample was treated in 10%  $\text{H}_2\text{O}_2$  solution, an initial sharp decrease in conductivity (25%) was observed within 50 h, then the sample conductivity tends to maintain a constant value of about 75% with no further decrease in conductivity again. Thus, it can be assumed that the PVA/QHECE alkaline membranes not only show high  $\text{OH}^-$  conductivity after oxidative treatment, but also possess excellent oxidative stability.

### 3.7. Methanol permeability

The DMFC have recently emerged as the technology of alternative energy for low temperature power applications. In DMFC, the methanol permeability ( $P_M$ ) is recognized as a key factor, which not

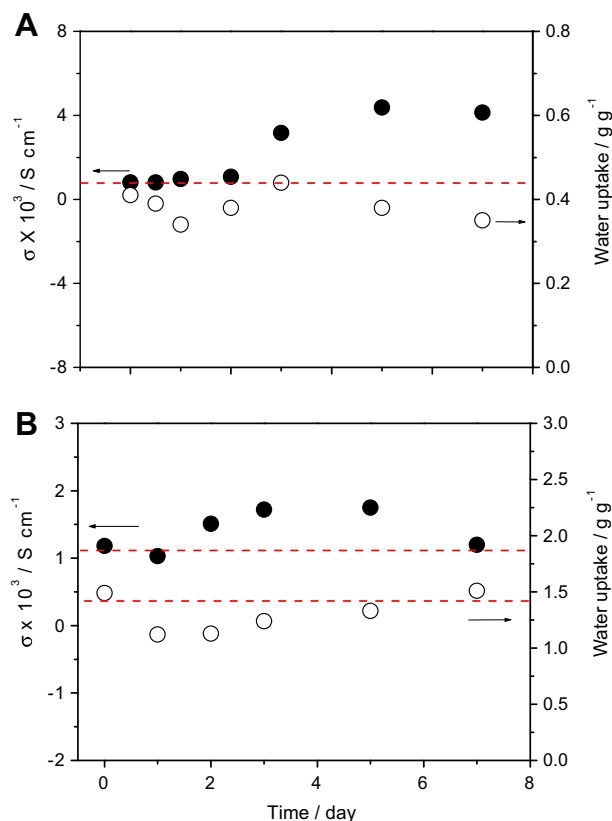


Fig. 9. Time course of WU and  $\text{OH}^-$  conductivity of PVA/QHECE alkaline membranes in 6.0 M KOH solution at  $80^\circ\text{C}$ . Membrane composition: (A) 1:0.125, (B) 1:1 by mass.

only causes loss of fuel but also reduces performance at the cathode due to the mixed reaction of methanol oxidation with the oxygen reduction reaction. Therefore, membranes that show high ionic conductivity, and at the same time, low methanol permeability are strongly desired. The relevant data of PVA/QHECE alkaline anion-exchange membranes and Nafion 115® membrane are shown in Table 1, where the concentration of methanol in the feed side was 3.0 M. It can be seen that  $P_M$  values of PVA/QHECE fall in the range from  $1.26$  to  $1.72 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which are much lower than that of Nafion 115® with a  $P_M$  value of  $2.35 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  measured in this

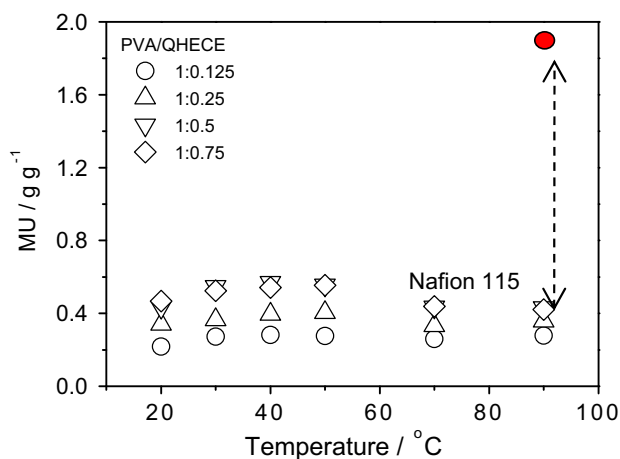


Fig. 8. Methanol uptake of PVA/QHECE alkaline membranes as a function of temperature.

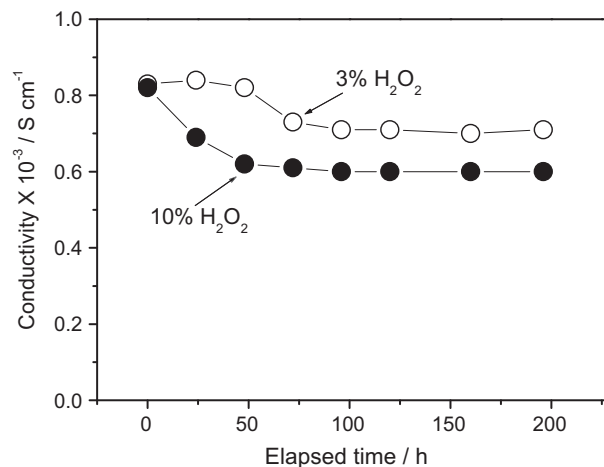
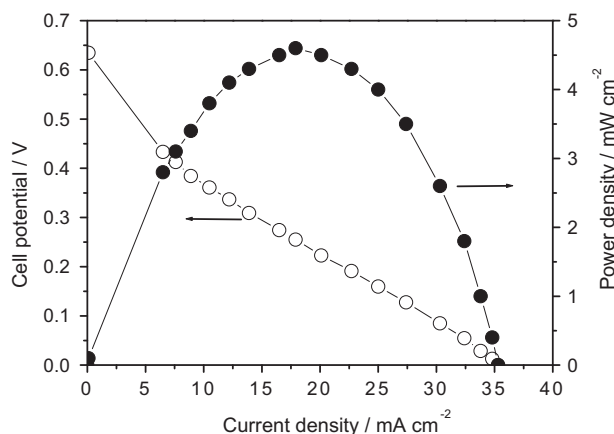


Fig. 10. Time course of  $\text{OH}^-$  conductivity of PVA/QHECE alkaline membrane in 3% and 10%  $\text{H}_2\text{O}_2$  solutions at  $60^\circ\text{C}$ . Membrane composition: 1:0.125 by mass.





**Fig. 11.** Polarization curve of DMAFC using PVA/QHECE (1:0.125 by mass) as alkaline anion-exchange membrane in 2.0 M KOH + 2.0 M CH<sub>3</sub>OH solution at the room temperature under ambient pressure (Pt-loading for anode and cathode: 0.5 mg cm<sup>-2</sup>).

work, that is, only 1/19 (PVA/QHECE = 1:0.25 by mass) and 1/14 (PVA/QHECE = 1:0.5 by mass) of that of Nafion<sup>®</sup>. Nafion<sup>®</sup> membrane has a hydrophobic flexible polymer backbone and sulfonic acid groups on its long flexible side chains, which forms distinct hydrophilic and hydrophobic domains. Through the hydrophilic domain, methanol is transported easily. On the contrary, in PVA/QHECE membranes the state of apparent hydrophilic and hydrophobic separation is not formed due to the complexed inter-network structure, thus the ion channel like the Nafion<sup>®</sup> membrane cannot be produced. In addition, as shown in Fig. 8 and Table 3 the PVA/QHECE membranes have much less affinity to methanol relatively to water than Nafion 115<sup>®</sup> owing to the high water selectivity of PVA and the ionized hydrate group of QHECE. Furthermore, the movement of OH<sup>-</sup> hinders the methanol permeability. All above afford the PVA/QHECE membranes perfect methanol resistance, which are very promising for application in DAMFC.

### 3.8. Single-cell performance

Fig. 11 shows the polarization curve of the DMAFC using PVA/QHECE (1:0.125 by mass) as alkaline anion-exchange membrane in 2.0 M KOH + 2.0 M CH<sub>3</sub>OH solution at the room temperature. As seen in Fig. 11, the PVA/QHECE membrane showed an initial peak power density around 4.6 mW cm<sup>-2</sup> and the maximum current density at 35 mA cm<sup>-2</sup>. The open circuit potential of the alkaline DMAFC was about 0.67 V. The value is comparable to that recorded for PVA/TiO<sub>2</sub> composite at 60 °C (7.54 mW cm<sup>-2</sup>) [31] and much higher than that of the fumasep<sup>®</sup> FAA-2 based AAEM (0.32 mW cm<sup>-2</sup>) [32] and QPVA/Q-SiO<sub>2</sub> (0.27 mW cm<sup>-2</sup>) [33] at room temperature. However, the performance is still low at this stage. This may be explained by the following two facts: (i) the OH<sup>-</sup> conductivity of the membrane is not high and (ii) the MEA fabrication conditions are not optimized. The poor chemical compatibility between the ionomer used (Nafion<sup>®</sup> ionomer) in the electrodes and the quaternary ammonium-type composite membrane is likely to be the cause of the poor performance observed. Chemical incompatibilities such as this can cause high contact resistances and poor MEA lamination. Another possible reason is the low Pt loading level of the anode and cathode (0.5 mg cm<sup>-2</sup>).

## 4. Conclusions

In this work, novel alkaline anion-exchange membranes from PVA/QHECE composites have been prepared using combined

blending and chemical cross-linking procedures. All the PVA/QHECE membranes show good thermal stability with onset degradation temperature high above 300 °C. The OH<sup>-</sup> conductivity of the membranes was found to increase with temperature but no apparent changes with water uptake and methanol uptake with temperature. The strong alkaline resistance stability of the membranes has been achieved in 6.0 M KOH at 80 °C without losing their integrity and OH<sup>-</sup> conducting behavior during a week of evaluation. In addition, PVA/QHECE membranes show very low methanol permeability, which is only 1/19 of that of Nafion 115<sup>®</sup>. A preliminary fuel cell test using PVA/QHECE (1:0.125 by mass) alkaline membrane in 2 M KOH + 2 M CH<sub>3</sub>OH solution showed a peak power density of 4.6 mW cm<sup>-2</sup> at room temperature. In short, further work is needed to improve the fuel cell performances such as by applying both chemical and physical cross-linking technique, addition of plasticizer, modification with other quaternized comonomers and, using quaternary ammonium-type ionomer for electrode fabrication as well as the optimization of hot pressing procedures (temperature and pressure).

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